

## **Copolymerization kinetics obtained by stopped-flow polymerization**

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### Summary

Ethylene-propylene copolymerization was carried out over  $MgCl_2$ -supported  $TiCl_4$  catalyst with two different reaction schemes; i.e., stopped-flow copolymerization(SFC) and continuously-purged copolymerization(CPC). The reactivity ratios for each monomer was evaluated by Fineman-Ross and Kelen-Tüdös methods. It was found that the SFC resulted in smaller value of ethylene reactivity ratio( $r_E$ ) and larger value of propylene reactivity ratio( $r_P$ ) than the CPC. This seems to be attributed to the different extent of interaction between catalytic titanium sites and aluminum alkyls, i.e. active site formation and its over-reduction.

### Introduction

The monomer reactivities in a particular polymerization reaction can be obtained by measuring their reactivity ratios in copolymerization reactions. These reactivity ratios are calculated from the correlation between the monomer compositions of the feed and of the product copolymer. However, it is very difficult to keep a constant monomer concentration in the reacting phase during the copolymerization reaction. Therefore, the continuously-purged copolymerization(CPC) system has been often used to maintain a constant monomer concentration, where the mixture of ethylene and propylene was continuously supplied under a total pressure of 1 atm. It is believed that the stopped-flow copolymerization(SFC) system, which was previously used by Keii et al.(1) and then modified by Terano et al.(2) for propylene polymerization, can be applied to observe a quasi-living polymerization state(below 1.0 sec) of ethylene-propylene copolymerization. The present communication reports some preliminary data concerning the instantaneous values of reactivity ratio obtained from the SFC system, which are to be compared with the average values of reactivity ratio obtained from the CPC system.

### Experimental

#### Catalyst preparation

The  $MgCl_2$ -supported catalyst used in this study was prepared by cogrinding 9.522g of anhydrous  $MgCl_2$  with 1.1 ml of  $TiCl_4$  and 1.20ml of ethyl benzoate(EB) (EB/ $MgCl_2$  mole ratio = 0.085) in a Fritsch Pulverisette ball mill (capacity:45ml; with five balls of 1.5cm diameter and three balls of 1.2cm diameter) at room temperature for 2hr. The catalyst with BET surface area of  $9m^2/g$  contained 3.80 wt% of titanium.

#### Copolymerization

##### 1) Stopped-flow copolymerization(SFC)

The polymerization apparatus used in this study is similar to the one reported by

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Keii et al.(1) and then modified by Terano et al.(2) for propylene polymerization. It consists of two flasks: One flask(A) contains 200 cm<sup>3</sup> of catalyst suspension in heptane and the other(B) contains 200 cm<sup>3</sup> of Al(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub> dissolved in ethylene- and/or propylene-saturated heptane. A water bath is equipped for each container to maintain the system at a constant temperature. The catalyst suspension in (A) was kept under nitrogen, because the contact of the catalysts used in the present study with ethylene or propylene causes cationic polymerization which proceeds without Al(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>. By applying a small pressure of nitrogen, the solutions in (A) and (B) are forced to flow out simultaneously through a teflon tube of 2 mm inner diameter. When the solutions meet at a simple three-necked joint(a), polymerization starts and continues until quenched by 400 cm<sup>3</sup> of ethanol contained in 1 dm<sup>3</sup> flask(C).

The polymerization was conducted at 30°C under a pressure of 1 atm with 0.5g of catalyst and the prescribed amount of Al(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>(Al/Ti mole ratio=5). The ethylene and propylene concentration was listed in Table 1. The polymerization time was 0.76 sec. Monomer conversions were found to be below 10 % under the present conditions. To the polymer suspension in ethanol, 400 cm<sup>3</sup> of water together with 20 cm<sup>3</sup> of HCl was added and stirred overnight. This was found to eliminate the catalyst residue in the product. After separating the polymer using the separatory funnel, it was dried in vacuum at 100°C.

## 2) Continuously purged copolymerization(CPC)

The polymerization procedure is similar to the one previously used by Soga et al.(3). Copolymerization of ethylene with propylene was carried out in 250 cm<sup>3</sup> glass reactor equipped with a magnetic stirrer. 0.1g of catalyst was suspended in 96 cm<sup>3</sup> of heptane under nitrogen atmosphere. After the temperature was raised up to 30°C, a mixture of ethylene and propylene was introduced at a flux of 2 l/min to assure a constant monomer concentration in the reacting phase into the reactor. After 10 min, the prescribed amount of Al(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>(4 cm<sup>3</sup> of heptane solution) was added to start the copolymerization. The mixture of ethylene and propylene was continuously supplied under a total pressure of 1 atm. The mole ratio of ethylene to propylene was changed by controlling the flow rate of each monomer. The concentrations of ethylene and propylene in heptane were calculated according to the vapor-liquid equilibrium using Chao-Seader correlation(4). The copolymerization was conducted at 30°C for 10 min and terminated by adding a dilute hydrochloric acid solution in ethanol. The product polymer was adequately washed with methanol and dried in vacuum.

## Polymer Characterization

The compositions of poly(ethylene-co-propylene) were estimated from the A<sub>7.25</sub>/A<sub>6.85</sub>μ absorbance ratios(5) of the IR spectrum(with a Bomem MB-102 Infrared Spectro photometer). The calibration curve for the absorbance ratios was obtained by using polypropylene-polyethylene blends dissolved in xylene.

The melting point of the copolymer was determined from the peak of the differential scanning calorimetric(DSC) spectra, measured with a Dupont apparatus. DSC measurements were made at a heating rate of 10°C/min. The samples were melted at 200°C, and the rescanned peaks were taken for analysis.

## Results and Discussion

Two types of copolymerization, SFC and CPC, were carried out at 30°C with the catalyst system, MgCl<sub>2</sub>/TiCl<sub>4</sub>/EB/Al(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>. For reference, homopolymerization of each olefin was conducted under similar conditions. The monomer reactivity ratios r<sub>E</sub> and r<sub>P</sub>(E = ethylene, p = propylene) were calculated according to the Fineman-Ross method and Kelen-Tüdös method(6), where the necessary parameters are defined as follows;

$$G = \frac{([m_E]/[m_P]-1) \cdot [M_E]/[M_P]}{[m_E]/[m_P]}$$

$$F = ([M_E]/[M_P])^2 / ([m_E]/[m_P])$$

where,

$$\frac{[M_E]}{[M_P]} = \frac{\text{Conc. of ethylene in heptane}}{\text{Conc. of propylene in heptane}}$$

$$\frac{[m_E]}{[m_P]} = \frac{\text{amount of ethylene in copolymer}}{\text{amount of propylene in copolymer}}$$

Fineman-Ross eq.

$$G = -r_P + r_E \cdot F$$

Kelen-Tüdös eq.

$$G/(F+\alpha) = (-r_P/\alpha) + (r_E+r_P/\alpha)(F/(F+\alpha))$$

where  $\alpha = (F_{\min} \cdot F_{\max})^{1/2}$

The results from two types of copolymerization are summarized in Tab. 1, 2, and 3. Tab. 1 shows the monomer concentration in the reacting medium and the propylene contents of the copolymer produced in the stopped-flow copolymerization (SFC) of ethylene and propylene together with the evaluation of some parameters for both Fineman-Ross and Kelen-Tüdös plots. Tab. 2 shows the results of the CPC for comparison with those of SFC in Tab. 1 under the similar conditions (Al/Ti = 5). The SFC gave the copolymers having slightly higher propylene unit contents at the same ethylene/propylene feed ratio than the CPC. In Tab. 1, homopolymerization rate

Table 1. Results of the stopped-flow copolymerization of ethylene and propylene together with the evaluation of some parameters (Al/Ti=5)<sup>a</sup>

Conc. of monomer in heptane [M <sub>E</sub> ], mol/l	[M <sub>P</sub> ], mol/l	P in copolymer <sup>b</sup> mol-%	G	F	G/(F+α)	F/(F+α)
0.0602	0.0067	1.156	8.896	0.947	7.352	0.783
0.0582	0.0147	3.014	3.876	0.497	5.100	0.654
0.0565	0.0242	4.569	2.222	0.261	4.240	0.498
0.0540	0.0360	6.943	1.388	0.168	3.220	0.390
0.0508	0.0509	11.268	0.873	0.127	2.238	0.326
0.0467	0.0701	14.252	0.556	0.0977	1.540	0.271
0.0412	0.0962	20.124	0.321	0.0731	0.955	0.217
0.0622	—	—	—	—	(α = 0.263)	
—	0.2889	Isotacticity <sup>c</sup> =n.a.(by extraction), above 95%(by IR)				

<sup>a</sup> Copolymerization conditions: Catalyst = 0.5g, Al/Ti = 5 mole ratio; each vol. of heptane = 200cm<sup>3</sup>; Total pressure = 1atm; T = 30°C; t = 0.76sec; E and P denote ethylene and propylene respectively.

<sup>b</sup> Calculated from IR spectra of copolymers.

<sup>c</sup> Isotacticity of polypropylene is defined by the fraction insoluble in boiling n-heptane for 6 hr and determined by A<sub>974</sub>/A<sub>995</sub> absorbance ratio of IR spectra, respectively(11).

constants  $k_{EE}$  and  $k_{PP}$ , could have been obtained from the SFC yield by measuring the number average molecular weight,  $\bar{M}_n$ . Our experiments carried out below 10% conversions did not produce the accurate and reproducible values of SFC yields due to the difficulty in separating small amount of products. Tab. 3 shows the results of the CPC when Al/Ti mole ratio is 30. This is to clarify the effect of Al/Ti mole ratio on the copolymerization characteristics in comparison with those in Tab. 2. The yield was strongly dependent upon the ratio of Al(C<sub>2</sub>H<sub>5</sub>) to titanium as to be shown later on in Fig. 3. It can be seen that the propylene content in the copolymer at Al/Ti=30 is slightly larger than at Al/Ti=5.

Table 2. Results of the continuously-purged copolymerization of ethylene and propylene together with the evaluation of some parameters(Al/Ti=5)<sup>a</sup>

Conc. of monomer in heptane		Yield P in copolymer <sup>b</sup>		G	F	G/(F+ $\alpha$ )	F/(F+ $\alpha$ )
[M <sub>E</sub> ],mol/l	[M <sub>P</sub> ],mol/l	in g	mol-%				
0.1204	0.0134	0.276	0.464	8.943	0.527	13.530	0.797
0.1170	0.0293	0.583	1.410	3.943	0.229	10.862	0.631
0.1129	0.0484	0.714	2.634	2.270	0.147	8.078	0.523
0.1079	0.0719	1.003	4.082	1.436	0.0958	6.249	0.417
0.1016	0.1017	1.908	5.550	0.941	0.0588	4.881	0.305
0.0934	0.1401	2.111	10.158	0.591	0.0503	3.207	0.273
0.0824	0.1923	2.189	15.595	0.349	0.0339	2.079	0.202
0.1243	—	0.092				( $\alpha = 0.134$ )	
—	0.5777	0.736	Isotacticity <sup>c</sup> =70.9%(by extraction), 83.0%(by IR)				

<sup>a</sup> Copolymerization conditions: Catalyst = 0.1g, Al/Ti = 5 mole ratio; each vol. of heptane = 100cm<sup>3</sup>; Total pressure = 1atm; T = 30°C; t = 10min; E and P denote ethylene and propylene respectively.

Table 3. Results of the continuously-purged copolymerization of ethylene and propylene together with the evaluation of some parameters(Al/Ti=30)<sup>a</sup>

Conc. of monomer in heptane		Yield P in copolymer <sup>b</sup>		G	F	G/(F+ $\alpha$ )	F/(F+ $\alpha$ )
[M <sub>E</sub> ],mol/l	[M <sub>P</sub> ],mol/l	in g	mol-%				
0.1204	0.0134	0.712	0.780	8.930	0.637	11.463	0.818
0.1170	0.0293	1.570	1.748	3.929	0.285	9.201	0.667
0.1129	0.0484	4.822	3.252	2.254	0.183	6.935	0.563
0.1079	0.0719	5.276	5.268	1.417	0.125	5.307	0.468
0.1016	0.1017	3.884	6.398	0.932	0.0684	4.430	0.325
0.0934	0.1401	2.616	9.060	0.600	0.0443	3.221	0.238
0.0824	0.1923	1.827	14.670	0.355	0.0316	2.045	0.182
0.1243	—	0.560				( $\alpha = 0.142$ )	
—	0.5777	1.780	Isotacticity <sup>c</sup> =63.7%(by extraction), 73.0%(by IR)				

<sup>a</sup> Copolymerization conditions: Catalyst = 0.1g, Al/Ti = 30 mole ratio; each vol. of heptane = 100cm<sup>3</sup>; Total pressure = 1atm; T = 30°C; t = 10min; E and P denote ethylene and propylene respectively.

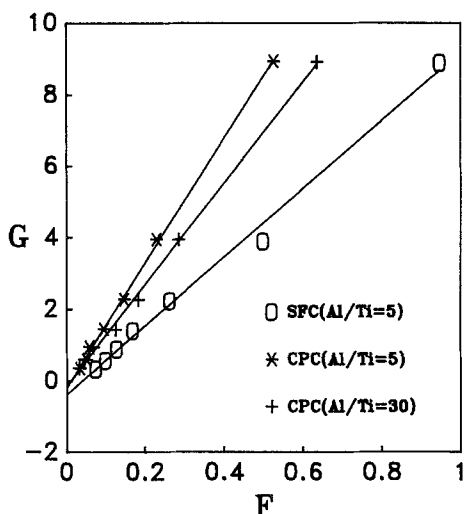


Figure 1 Fineman-Ross plots: o; for SFC, \*; for CPC(Al/Ti=5), +; for CPC(Al/Ti=30).

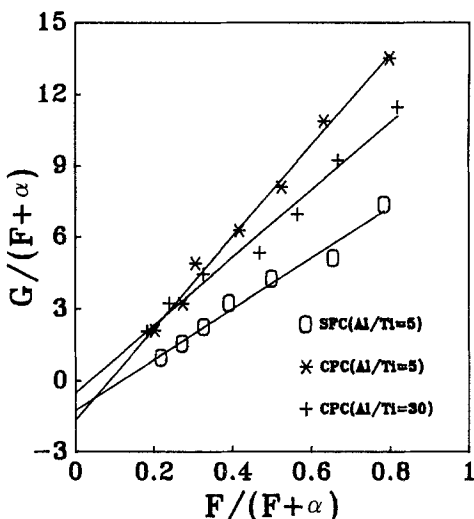


Figure 2 Kelen-Tüdös plots: o; for SFC, \*; for CPC(Al/Ti=5), +; for CPC(Al/Ti=30).

Using the values of parameters,  $F$ ,  $G$  and  $\alpha$  in Tab. 1, 2, and 3, both Fineman-Ross and Kelen-Tüdös plots for the two types of copolymerizations are given in Fig. 1 and 2. The monomer reactivity ratios calculated from these plots are listed in Tab. 4, together with the isotacticity values of polypropylene produced. Good linearity was obtained for Fineman-Ross plots as well as Kelen-Tüdös plots. Both plotting methods provided almost the same reactivity ratios. The propylene reactivity ratio  $r_p$  in SFC is about two times larger than that in CPC. This is expected because the propylene content in the copolymer is higher in SFC than in CPC for the same feed composition as shown in Tab. 1, 2, and 3. It is of interest to note in the Tab. 4 that the value (3.64) of  $r_{E_P}$  for the SFC was higher than that (3.57 for Al/Ti=5) for CPC, and also the value (3.57) for Al/Ti=5 was higher than that (2.1) for Al/Ti=30 in CPC. Thus the distribution of the ethylene and propylene monomer units is expected to be more blocky for the SFC than for the CPC(7).

Table 4. Evaluation of monomer reactivity ratios

Type of Copolymn	$r_E$		$r_P$		Isotacticity <sup>b</sup> (%)	
	Fineman-Ross	Kelen-Tüdös	Fineman-Ross	Kelen-Tüdös	Extraction	IR
Stopped-flow copolymn	9.6	9.4	0.38	0.33	n.a.	>95
Continuously-purged copolymn <sup>a</sup>	(a) 17.4	17.6	0.21	0.23	70.9	83
	(b) 14.2	13.7	0.15	0.075	63.7	73

<sup>a</sup> (a) For Al/Ti=5 and (b) For Al/Ti=30

<sup>b</sup> Isotacticity of polypropylene is defined by the fraction insoluble in boiling n-heptane for 6 hr and determined by  $A_{974}/A_{995}$  absorbance ratio of IR spectra, respectively(11).

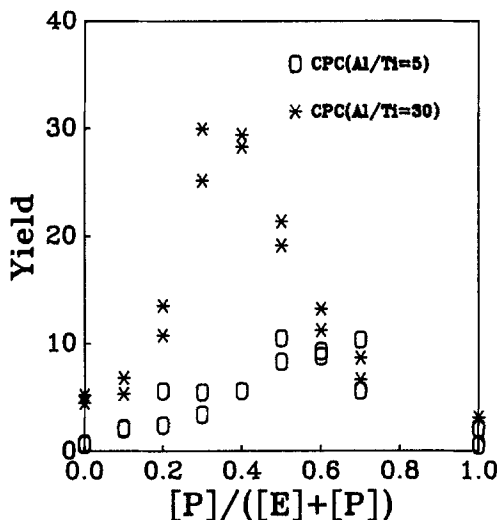


Figure 3 Yield [total polymer(g)/amount of monomers dissolved in heptane ([E]+[P])] as a function of monomer composition. Polymerization conditions are the same as those in Tab. 2 and 3, respectively: o; for Al/Ti=5, \*; for Al/Ti=30, E and P denote ethylene and propylene, respectively.

The yield was strongly dependent upon the ratio of  $\text{Al}(\text{C}_2\text{H}_5)_3$  to titanium as shown in Fig. 3. It is often observed in ethylene polymerization using Ziegler-Natta catalysts that addition of a small quantity of propylene monomer markedly increases the apparent polymerization activity. The results are often explained by the assumption that the propagation rate constants of the cross reactions are very high(8). On the other hand, the increased rates of ethylene polymerization might be explained by an increase of monomer diffusion through less crystalline copolymer film due to incorporation of comonomer as described by Soga et al.(9) From Fig. 3., it is shown that the apparent polymerization activity shows a maximum. It is recognized that the polymerization activity, or more precisely, the propagation rate, of ethylene is much higher than that of propylene. However, the ethylene activity was not so much high for Al/Ti=5 and slightly higher for Al/Ti=30 than the propylene activity. It is expected that as Al/Ti mole ratio increases, the ethylene activity becomes higher than the propylene activity and the maximum activity will shift to the lower range of comonomer content.

The values of the heat of fusion,  $\Delta H_f$  and the melting point,  $T_m$  for the copolymers shown in Fig. 4. and Fig. 5. are very typical for ethylene copolymers in this composition range. Their values in SFC were always higher than those in CPC. That is to say, the crystallinity of the copolymer obtained by SFC was always larger than those obtained by CPC for the same comonomer content in the copolymer. It is expected that the crystallinity be smaller for higher comonomer content in the copolymer. But the crystallinity will be affected by various factors, such as the comonomer distribution and its configuration in the copolymer chain as well as its content. The above experimental results might be well explained as the following bases(12). The nature of active sites in heterogeneous Ziegler-Natta catalyst is essentially not uniform. These active sites might be largely classified to three kinds of sites, that is, isospecific titanium(III) site, aspecific titanium(III) site and ethylene-favorable titanium(II) site. In the SFC with low Al/Ti mole ratio, there might exist only the isospecific site which polymerizes olefins to the stereospecific, highly crystalline copolymer. But in the CPC there might exist large amount of ethylene-favorable titanium(II) site as well as titanium(III) sites. And also as Al/Ti mole ratio increases, the isospecific titanium(III) sites might be transformed to the aspecific titanium(III) sites due to the extraction of ethyl benzoate by  $\text{Al}(\text{C}_2\text{H}_5)_3$ . Aspecific site is well known to be more favorable to the incorporation of comonomer into the polymer chain than isospecific site(13). This logic might be supported by the isotacticity data as shown in Tab. 4.

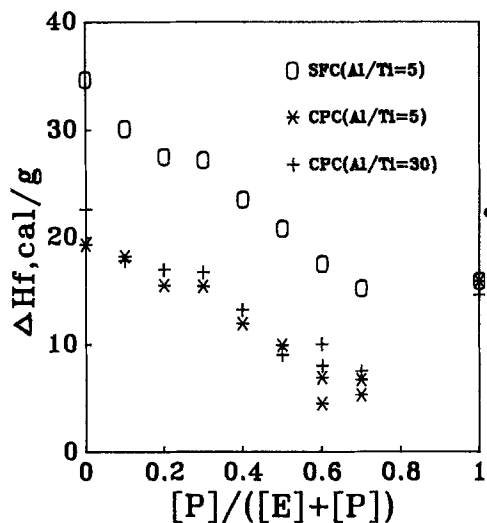


Figure 4 Heat of fusion of polymers as a function of monomer composition: o; for SFC, \*; for CPC(Al/Ti=5), +; for CPC(Al/Ti=30).

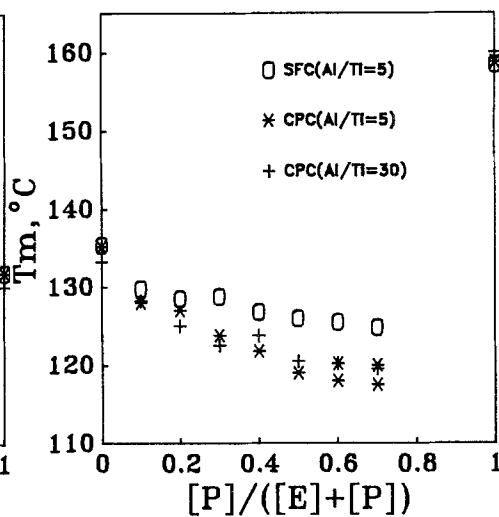


Figure 5 Melting point of polymers as a function of monomer composition: o; for SFC, \*; for CPC(Al/Ti=5), +; for CPC(Al/Ti=30).

In conclusion, it was found that the SFC resulted in smaller value of ethylene reactivity ratio ( $r_E$ ) and larger value of propylene reactivity ratio ( $r_P$ ) than the CPC. A more detailed study on the polymer structure (e.g. by  $C^{13}NMR$ ) is now being carried out and the results of Al/Ti mole ratio and the aging effect will be reported in full detail in another paper.

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